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(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventors: MARTENS, John, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). STAUS, Gary, A.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). WANG, Paul, J.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(74) Agents: SKOLNICK, Steven, E. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

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(54) Title: MULTILAYER FLEXOGRAPHIC PRINTING PLATE

(57) Abstract

This invention provides a process for producing a multilayer, flexible photosensitive plate comprising (i) applying a first photosensitive elastomeric layer to a flexible substrate, (ii) curing the first photosensitive elastomeric layer by exposure to actinic radiation, and (iii) following this curing, applying a second layer, which is at least 0.2 mm thick, onto the first photosensitive layer, the second layer comprising a photosensitive elastomeric composition having no more than 1 % by weight ethylenically unsaturated copolymerizable molecules with molecular weights less than 300. This multilayer photosensitive plate may be used as a flexographic printing plate if imagewise exposed and developed. These multilayer plates are particularly suitable for thermal development.

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MULTILAYER FLEXOGRAPHIC PRINTING PLATE

Background

1. Field of the Invention

The present invention relates to multilayer flexographic printing plates.

2. Background of the Invention

Flexography is a term broadly applicable to a printing format that uses a flexible substrate bearing an elastomeric or rubbery relief printing surface. The first flexographic printing plates were produced from natural or synthetic rubber compositions which were cured chemically under heat and pressure in a mold utilizing conventional rubber curatives such as mercapto compounds (*Flexography: Principles and Practices*, 3rd Edition, Flexographic Technical Association, p. 158-162). More recently, photopolymer elastomeric compositions (elastomer containing compositions curable upon exposure to actinic radiation) have been used to produce relief printing plates. For example, U.S. Patent 4,162,919 describes the use of a photosensitive composition containing a block copolymer as an elastomeric polymeric binder, a compatible ethylenically unsaturated monomer, and a photoinitiator. Similarly, British Patent 1,454,191 describes the use of an elastomeric polyurethane based photosensitive layer. In both cases, the standard solvent wash procedure is used to develop the relief layer after exposure to actinic radiation. European Patent 261,910 describes an aqueous-developable flexographic printing plate.

U.S. Patents 3,948,665 and 4,162,919 and British Patent 1,454,191 describe flexographic plates which, in addition to the relief layer and the substrate, contain an elastomeric layer for purposes of adjusting hardness. All three patents relate to solvent wash developable systems.

Both the solvent wash and aqueous wash developing systems are time consuming since drying for extended periods (1 to 24 hours) is necessary to remove entrained developer solution. In addition, these developing systems produce potentially toxic by-product wastes (both the solvent and any material carried off by the solvent, such as unreacted ethylenically unsaturated monomer) during the development process.

To avoid these problems, a thermal development process may be used. In a thermal development process, the photosensitive layer, which has been image-wise exposed to actinic radiation, is contacted with an absorbent layer at a temperature sufficient to cause the composition in the unexposed portions of the photosensitive layer to soften or melt and flow into the absorbent material. See U.S. Patent No. 3,264,103 for planographic development and U.S. Patent No. 5,015,556 for relief development. One drawback to this process is the emission of volatiles (such as unreacted monomer) during thermal development.

An additional processing step that is frequently used in producing flexographic printing plates is irradiating the photosensitive, elastomeric layer of the plate with ultraviolet radiation or electron beam (e-beam) radiation through the flexible substrate. This process is described in U.S. Patents No. 5,215,859, 4,264,705, 5,015,556, and 4,927,723. The photosensitive layer is thereby partially cured forming a "floor" which is not removed during development.

Unfortunately, neither ultraviolet nor e-beam radiation through the substrate is entirely satisfactory for flexographic printing plates produced by thermal development. Ultraviolet backflashing is problematic because it is difficult to control the extent and depth of cure. A back flash that is of too short a duration provides an insufficient anchor for the relief image,

and the resulting image may break off from the base of the printing plate. On the other hand, if the backflash is maintained too long, the top of the photosensitive layer begins to cure and becomes too viscous to be developed thermally. Slight overcuring is not a serious detriment in solvent or aqueous developing systems because generally the solvent or aqueous solution is brushed on and that brushing smoothes the surface and helps remove particles still adhering to the imaged plate. However, in thermally developed systems, it has been found that UV backflashing does not allow for good clean-out of the nonirradiated areas of the printing plate.

The use of electron beam irradiation to set the floor provides more consistent results as compared to UV radiation. The penetration of the electron beam into the plate can be precisely controlled by selection of the proper accelerating voltage of the electrons. The use of electron beam is suggested when relatively thin (<1.2 mm) flexographic printing plates are desired. However, electron beams are impractical for producing adequate floors for the frequently desired thicker plates (> 1.2 mm) due to the inordinately high accelerating voltages required (>300 KeV) to achieve adequate penetration depth into the plate.

Summary of the Invention

This invention provides a multilayer flexible plate suitable for use as a thermally developable flexographic printing plate and a process for making that plate.

According to one embodiment, this invention provides a process for producing a multilayer, flexible photosensitive plate comprising (i) applying a first photosensitive elastomeric layer to a flexible substrate, (ii) curing the first photosensitive elastomeric layer by exposure to actinic radiation, and (iii) following this curing, applying a second layer, which is at least 0.2 mm thick, onto the first photosensitive layer, the second layer comprising a photosensitive elastomeric composition having no more than 1% by weight

ethylenically unsaturated copolymerizable molecules with molecular weights less than 300.

In a second embodiment, the invention is a multilayered, flexible photosensitive plate comprising

A) a flexible substrate,

B) a first photosensitive elastomer layer which has been cured by exposure to radiation, and

C) a second photosensitive elastomeric layer at least 0.2 mm thick having no more than 1% by weight ethylenically unsaturated copolymerizable molecules with molecular weights less than 300.

In yet another embodiment, the invention provides a process for producing a multilayered flexographic printing plate comprising:

(i) applying a first photosensitive, elastomeric layer to a flexible substrate,

(ii) curing the elastomeric composition by exposure to radiation,

(iii) applying a second layer at least 0.2 mm thick onto the first elastomer layer, the second layer comprising a photosensitive curable elastomer composition having no more than 1% by weight ethylenically unsaturated copolymerizable molecules with molecular weights less than 300,

(iv) image-wise exposing the second photosensitive, elastomeric layer to ultraviolet radiation, and

(v) developing the printing plate by contacting the image-wise exposed photosensitive elastomeric layer with an absorbent material at a temperature sufficient to enable unexposed portions of the photosensitive layer to flow into the absorbent layer.

The invention is also embodied by a flexographic printing plate made according to this procedure. The flexographic printing plate comprises a substrate, a floor layer in which the degree of cure is constant in a plane perpendicular to the substrate, and an image bearing relief layer. The flexographic printing plates of this invention have a well defined image and good clean out of non-irradiated areas.

Detailed Description of the Invention

The process of the present invention comprises applying a first layer of a photosensitive, elastomeric composition onto a flexible substrate, curing the elastomeric composition by exposure to actinic radiation, and, following the curing of the first layer, applying a second photosensitive elastomeric layer with a low content of volatiles onto the cured first layer.

The substrate may be any flexible material including metal sheets, thermoplastic films, open or closed celled foams, compressible rubber, or some combination of the preceding materials. Thermoplastic films, especially polyester films such as polyethylene terephthalate (PET), are well suited for use as the flexible substrate. The substrate is preferably annealed according to the methods described in WO 91/14603. The substrate optionally may be surface treated for better adhesion. One example of such a surface treatment is corona treating the surface followed by use of a primer such as an aziridene functional material. The substrate may be 0.075 to 2 mm thick and is preferably 0.1 to 1.5 mm thick.

The compositions of the two photosensitive layers may be identical. However, according to some preferred embodiments the compositions of the two photosensitive layers are at least slightly different from each other. The photosensitive elastomeric layers may be applied by any of the conventional methods for applying a film layer to a substrate, including lamination, knife coating, roller coating, extrusion, and the like. We turn

now to a discussion of the first and second photosensitive elastomeric layers.

First Layer (or Floor Layer)

The first layer is preferably cured before the addition of the second layer. Curing the first layer allows for a well defined image and a smooth floor following imagewise exposure and thermal development of the flexographic printing plate. Such curing of the first layer before addition of the second photosensitive layer also facilitates control of the floor thickness. Floor thickness may now be set merely by changing the thickness of the first layer. The thickness of the first layer is preferably at least 0.1 mm, more preferably in the range from about 0.5 mm to about 3.0 mm.

The degree of cure of the first layer must be such that the layer will not be removed during thermal development. Thus, the first layer may be fully cured or crosslinked. However, it may be desirable that the first layer is not completely crosslinked during cure, since adhesion between the first and second layers will be improved if the first layer was not fully crosslinked until after application of the relief forming layer. In one embodiment, the first layer is cured by exposing the top of the layer and the bottom of the layer (through the substrate) to actinic radiation. The curing of the top and bottom may be performed sequentially or simultaneously.

In one preferred embodiment, the cured, first photosensitive, elastomeric layer comprises a thermoplastic elastomeric block copolymer; a crosslinking agent; and a photoinitiator. The elastomeric block copolymer is preferably an A-B-A type block copolymer, where A is a nonelastomeric block, preferably a vinyl polymer and most preferably polystyrene and B is an elastomeric block, preferably polybutadiene or polyisoprene. The nonelastomer to elastomer ratio is preferably in the range of 10:90 to 35:65. Styrene-isoprene-styrene block copolymers are

especially preferred. The amount of thermoplastic elastomeric block copolymer present in the first layer is preferably in the range of from about 20 to about 90 parts by weight based on the total weight of the layer. More preferably, the amount of block copolymer present is in the range of from about 60 to about 90, most preferably, from about 65 to about 85, parts by weight based on the total weight of the layer.

The crosslinking agent used in the first layer is preferably an ethylenically unsaturated compound with at least one terminal ethylenic group. Suitable compounds include multi-functional acrylates and methacrylates. Such compounds are typically present in amounts ranging from about 3 to about 50 parts by weight based on the total weight of the first layer. Preferably, they are present in amounts ranging from about 3 to about 20 parts by weight based on the total weight of the first layer. More preferably, they are present in amounts ranging from about 5 to about 10 parts by weight. The following compounds are illustrative of, but not an exhaustive list of, suitable crosslinking agents: ethoxylated bisphenol-A di(meth)acrylates, ethylene glycol diacrylate, hexanediol diacrylate, diethylene glycol diacrylate, glycerol diacrylate, trimethylol propane triacrylate, hexanediol dimethacrylate, glycerol triacrylate, trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, and 1,4-butanediol diacrylate. For a more exhaustive list of suitable compounds see U.S. Patent 4,400,459. A mixture of mono-functional and multi-functional ethylenically unsaturated compounds may be used. However, if using such a mixture, it is desirable to have an average of at least 1.3 ethylenically unsaturated groups per molecule of crosslinking agent. It is more preferable to have an average of at least 1.7 ethylenically unsaturated groups per molecule of crosslinking agent, and it is most preferable to have 2.0 ethylenically unsaturated groups per molecule of crosslinking agent.

The crosslinking agent may alternatively comprise an oligomer having more than one ethylenically unsaturated group such as an acrylate or vinyl group. Examples of such oligomers include acrylate-terminated polybutadiene, acrylate-terminated polyurethane, vinyl-terminated polybutadiene, and acrylate-terminated polyisoprene. The ethylenically unsaturated oligomer may be used in combination with a crosslinking agent having a molecular weight that is less than that of the oligomer. If this combination is used, the relative amounts of the block copolymer and the crosslinking agent may have to be adjusted. Such an adjustment is important because the photosensitive composition cannot be so stiff or viscous that it is unprocessable, yet it must also not be so runny that it flows during storage.

In the particular case where the crosslinking agent comprises an oligomer having more than one vinyl group, it is preferable to use an additional crosslinking agent therewith. More specifically, it is preferable to use an oligomer having more than one vinyl group in combination with a crosslinking agent having more than one acrylate group and a molecular weight greater than 300 but less than 1000. It has been discovered that when the oligomer having more than one vinyl group is used alone, the cure rate of the resulting elastomeric layer is retarded. The use of the additional crosslinking agent (having more than one acrylate group and a molecular weight greater than 300 but less than 1000) surprisingly eliminates this problem of retarded cure.

When used, oligomers are typically present in amounts ranging from about 10 to about 50 parts by weight based on the total weight of the first layer. Preferably, they are present in amounts ranging from about 15 to about 35 parts by weight based on the total weight of the first layer. In the particular case where the crosslinking agent comprises the combination of an oligomer having more than one vinyl group and a crosslinking agent (having more than one acrylate group and a molecular weight greater than 300 but less than 1000), the former is preferably

present in amounts ranging from about 10 to 50 (more preferably from about 15 to about 35) parts by weight, while the latter is preferably present in amounts ranging from about 3 to 15 (more preferably from about 5 to about 10) parts by weight based on the total weight of the first layer.

The photoinitiator is a compound which generates free radicals upon exposure to actinic radiation. Any of the known classes of photoinitiators, particularly free radical photoinitiators such as quinones, benzophenones, benzoin ethers, aryl ketones, peroxides, biimidazoles, diaryliodoniums, triarylsulfoniums and phosphoniums, diazoniums, etc. Alternately, the photoinitiator may be a mixture of compounds, one of which provides the free radicals when caused to do so by a sensitizer activated by radiation. The amount of photoinitiator present is typically in range of from about 0.5 to about 5 parts by weight based on the total weight of the first layer. Preferably, the amount of photoinitiator present is in the range of from about 1 to about 3 parts by weight, more preferably from about 1.5 to about 2.5 parts by weight.

Additional additives, such as colorants, processing aids, antiozonants, spectral sensitizers, and antioxidants, may be added if desired. Processing aids may be such things as low molecular weight polymers compatible with the elastomeric block copolymer, such as a low molecular weight a-methylstyrene polymer or copolymer, or fluorinated surfactants. Diene copolymers (such as polyisoprene and polybutadiene) and block copolymer of dienes (such as polyisoprene-polybutadien block copolymers) may also be added to improve melt flow properties and vary hardness. Antiozonants include hydrocarbon waxes, norbornenes, and vegetable oils. Antioxidants include alkylated phenols, alkylated bisphenols, polymerized trimethyldihydroquinone, and dilauryl thiopropinoate.

Second Layer (or Relief Forming Layer)

The second layer preferably is at least 0.2 mm thick and more preferably has a thickness in the range from about 0.4 mm to about 1.5 mm. The second photosensitive layer has a low content of volatiles. This reduces the amount of volatiles which are emitted during thermal development. The second photosensitive layer preferably contains less than 1.0%, more preferably less than 0.5%, and most preferably less than 0.1% by weight ethylenically unsaturated copolymerizable molecules with molecular weights under 500, more preferably under 300. Limiting the amount of other materials which may volatilize during thermal development is also advisable. Many photoinitiators can be found which will not volatilize during thermal development, and such compounds are preferred. Similarly, many dyes or pigments can be safely employed without increasing the emission of volatiles. Inorganic additives, antioxidants, antiozonants, and the like generally will not volatilize during thermal development, but those that do should be used only in limited amounts or avoided entirely if possible.

The second photosensitive, elastomeric layer preferably comprises 20 to 80, more preferably 40 to 60, parts by weight of a thermoplastic elastomeric block copolymer. This block copolymer may be the same as was used in the cured first layer. Preferably, the second photosensitive, elastomeric layer further comprises 10 to 50 (more preferably 15 to 45) parts by weight of an oligomer having more than one ethylenically unsaturated group such as an acrylate or vinyl group. Examples of such oligomers include acrylate-terminated polybutadiene, acrylate-terminated polyurethane, vinyl-terminated polybutadiene, and acrylate-terminated polyisoprene. Preferably the oligomer has a molecular weight greater than 1000, more preferably the molecular weight is greater than 2000, and most preferably the molecular weight of the oligomer is greater than 3000. The oligomer is preferably devolatilized so that less than 500, preferably less

than 300, and most preferably less than 150 parts per million of residuals (such as by-products of polymerization or monomers) remain. This oligomer serves as the crosslinking agent for the relief layer. An oligomer is preferred over a low molecular weight compound to enable thermal development of the flexographic printing plate without emission of toxic volatiles that would be present in the unexposed regions if a lower molecular weight material is used. The ratio by weight of oligomeric crosslinking agent to elastomeric block copolymer is usually higher than is needed if a lower molecular weight crosslinking agent is used. The higher ratio is needed to keep the viscosity of the relief plate low enough for effective thermal development.

As described previously, in the particular case where the crosslinking agent comprises an oligomer having more than one vinyl group, it is preferable to use an additional crosslinking agent therewith. More specifically, it is preferable to use an oligomer having more than one vinyl group in combination with a crosslinking agent having more than one acrylate group and a molecular weight greater than 300 but less than 1000. It has been discovered that when the oligomer having more than one vinyl group is used alone, the cure rate of the resulting elastomeric layer is retarded. The use of the additional crosslinking agent (having more than one acrylate group and a molecular weight greater than 300 but less than 1000) surprisingly eliminates this problem of retarded cure.

The oligomeric crosslinking agents are typically present in amounts ranging from about 10 to about 50 parts by weight based on the total weight of the second layer. Preferably, they are present in amounts ranging from about 15 to about 35 parts by weight based on the total weight of the second layer. In the particular case where the crosslinking agent comprises the combination of an oligomer having more than one vinyl group and a crosslinking agent (having more than one acrylate group and a molecular weight greater than 300 but less than 1000), the former is preferably present in amounts ranging from about 10 to 50 (more

preferably from about 15 to about 35) parts by weight, while the latter is preferably present in amounts ranging from about 3 to 15 (more preferably from about 5 to about 10) parts by weight based on the total weight of the second layer.

This photosensitive curable relief layer further comprises a photosensitive free radical initiator such as those already described for the first layer. The amount of photoinitiator present is typically in range of from about 0.5 to about 5 parts by weight based on the total weight of the second layer. Preferably, the amount of photoinitiator present is in the range of from about 1 to about 3 parts by weight, more preferably from about 1.5 to about 2.5 parts by weight.

As in the cured first elastomeric layer, the photosensitive curable relief layer may also contain processing aids, antiozonants, antioxidants, and the like. As noted previously, however, additives which volatilize during thermal development should be used only in limited amounts or avoided entirely if possible. In addition, additives which have a tendency to migrate in the presence of ink or the solvents used to clean the plates should also be used sparingly or avoided entirely if possible.

In another embodiment, the cured first layer comprises a photosensitive curable elastomeric polyurethane. This polyurethane is the reaction product of (i) an organic diisocyanate, (ii) at least one chain extending agent having at least two free hydrogen groups capable of polymerizing with isocyanate groups and having at least one ethylenically unsaturated addition polymerizable group per molecule, and (iii) an organic polyol with a minimum molecular weight of 500 and at least two free hydrogen containing groups capable of polymerizing with isocyanate groups. This first layer is cured by exposure to actinic radiation. A second photosensitive curable elastomeric polyurethane layer is then extruded onto the cured first layer. This second photosensitive layer is the reaction product of (i) an organic diisocyanate, (ii) at least one chain extending agent having at least two free hydrogen groups capable of polymerizing

with isocyanate groups and having at least one ethylenically unsaturated addition polymerizable group per molecule, and (iii) an organic polyol with a minimum molecular weight of 500 and at least two free hydrogen containing groups capable of polymerizing with isocyanate groups. For a more complete discussion of these materials see U.S. Patent 5,015,556. Again processing aids, antiozonants, antioxidants and other desired additives may be used.

Optionally, a hardcap layer may be provided on top of the photosensitive curable relief layer. The hardcap layer is typically a photosensitive elastomeric composition. Frequently, the binder of the hardcap layer is the same as or similar to the composition of the photosensitive relief layer with the addition of a pigment.

An antistatic layer added above the relief layer or the pigment layer may be used. This antistatic layer may comprise such materials as vanadium pentoxide, quaternary ammonium compounds or other materials or layers that can be removed during thermal development.

A cover film may also be added on top of the relief layer to prevent the image bearing film used in imagewise exposing the flexographic plate from sticking to the flexographic plate. For example, cover films comprising polyamides or hydroxyalkyl cellulose may be used. In addition, a protective cover layer may be used on top of the plate. This protective layer must be easily removable, because it is removed prior to imagewise exposure of the flexographic printing plate. The cover layer or protective may be a variety of materials including plastic films (e.g., polyester) or polymer coated paper.

The process of the present invention may further comprise image-wise exposure of the photosensitive curable layer of the flexographic printing plate to actinic radiation, preferably ultraviolet radiation. The exposed plate may then be developed by contacting the exposed photosensitive layer to an absorbent surface at a temperature sufficient to

cause the unexposed portions of the plate to melt and flow into the absorbent surface.

The resulting flexographic printing plate has a well defined image and good clean-out of the non-irradiated areas to leave a clean floor. A clean floor, according to the present invention, as compared to the floor produced on flexographic plates by means of backside curing from ultraviolet or e-beam radiation, is substantially smooth without visible irregularities beyond a slight, consistent texture on the floor surface. The smooth floor is believed to result because the substitution of a preliminary curing step of the first layer for the traditional backflashing method for setting the floor allows for an even or relatively constant degree of cure in planes in the first layer which are perpendicular to the plane of the substrate. Since the curing in these planes is generally uniform, the degree of cure of the floor layer at the interface between the floor layer and the non-irradiated portions of the second layer is discontinuous or different. Cure may be measured by such techniques as gel fraction or percentage swell in a good solvent for the uncured material. For example, THF (tetrahydrofuran) is known to be a good solvent for the S-I-S block copolymer. Thus, material is more evenly removed during thermal development yielding a smoother floor.

Examples

Example 1

A roll of 7 mil (0.18 mm) polyethylene terephthalate (PET) (Layer A) was corona treated in air and coated with CX-100, an aziridine functional compound in isopropyl alcohol from Polyvinyl Chemical Co. A 2 mil (0.05 mm) dry adhesive layer (B) was laminated to the substrate. A 36 mil (0.91 mm) photosensitive curable elastomer composition (C) was laminated to the adhesive layer. Layer C was then exposed to ultraviolet light for 30 seconds from the top and 30 seconds from the bottom through

the substrate to cure the photopolymer. A 36 mil (0.91 mm) photosensitive curable elastomer layer (D) was laminated to the cured polymer layer.

A 4 mil (0.1 mm) polyester film (G) was laminated with a release layer (F) and a hardcap layer (E). This multilayer structure was then laminated to the above structure so that layers D and E contacted each other.

Layer compositions:

A - aziridine coated PET.

B - 80% (by weight) KRATON 1117 (styrene-isoprene-styrene (SIS) block copolymer from Shell Chemical Co.)
1.6% IRGACURE 651 (acetophenone photoinitiator from Ciba-Geigy)
8.4% PICOTEX 75 (a-methylstyrene/vinyl toluene copolymer from Hercules)
4.0% hexanediol diacrylate
3.0% trimethylol propane triacrylate
3.0% hexanediol dimethacrylate

C - 65.9% KRATON 1117
24.4% polybutadiene diacrylate Poly BD-300 (Atochem)
1.2% IRGACURE 651
3.4% PICOTEX 75
3.4% SYNTENE 160 hydrocarbon wax (C&C Petroleum)
1.0% antioxidant (IRGANOX 1076 (Ciba-Geigy) and CYANOX LTDP (American Cyanamid))

D - 65.9% KRATON 1117
24.4% polybutadiene diacrylate
1.2% IRGACURE 651
3.4% PICOTEX 75
3.4% SYNTENE 160 hydrocarbon wax
1.0% antioxidant (IRGANOX 1076 and CYANOX LTDP)

E - 4% pigment in a binder layer with the composition the same as layer D.

F - hydroxypropyl cellulose

G - PET

Example 2

The multi-layer flexible plates from Example 1 were imagewise exposed and developed as follows. Layer G was removed and a negative image bearing film was placed against the release layer F. To produce reverse images on the plate, exposure to UV radiation was 3 minutes. To produce a bar code pattern, exposure to UV radiation was 9 minutes. For other patterns, exposure through a negative film occurred for 15 minutes. After exposure, the plates were developed by contact with an absorbent material at an elevated temperature. The absorbent material used was CEREX Type 23, a spunbonded nylon 6,6 non-woven material available from CEREX America, Inc. Both the absorbent material and the image exposed plates were attached to heated transport elements. The element carrying the absorbent material was maintained at approximately 175°C, while the temperature of the element carrying the flexographic plate was at about 60°C. After 10 contacts a flexographic printing plate exhibiting a clean, smooth floor with 36 mil (0.91 mm) relief and 38 mil (0.97 mm) floor was obtained.

Example 3

A roll of 7 mil (0.18 mm) polyethylene terephthalate (PET) (Layer A) film was corona treated in air and coated with CX-100, an aziridine functional compound in isopropyl alcohol from Polyvinyl Chemical. The web was dried at about 100°C to give a coating thickness of several hundred angstroms. Layer B was then blended and extruded from a twin screw extruder to produce a 35 mil (0.89 mm) coating of a photosensitive composition. This photosensitive layer B was cured by simultaneously exposing the top of the layer and bottom of the layer (through the substrate) to UV-radiation. Subsequently, a second photosensitive composition (layer C) was extruded onto the cured layer B producing a 25 mil (0.63 mm) layer. The ingredients of layer B were in weight percent:

80.3% SIS block copolymer
10.0% ethoxylated bisphenol A diacrylate

7.4% poly(alphamethylstyrene/vinyl toluene)
0.5% antioxidant
1.3% IRGACURE 651
0.5% hydrocarbon wax

The composition of layer C in weight % was:

55.3% SIS block copolymer
35.0% polybutadiene diacrylate
7.4% poly(alphamethylstyrene/vinyl toluene)
0.5% antioxidant
1.3% IRGACURE 651
0.5% hydrocarbon wax

A 5 mil (.13 mm) polyester film (E) was coated with a 0.2% solution of vanadium pentoxide. The vanadium pentoxide solution was prepared from 0.1% vanadium pentoxide and 0.1% surfactant in de-ionized water. After drying, the coating weight was 15 mg/m^2. To the coated film E was added a coating (D) of a 10% polyamide solution in n-propyl alcohol and toluene. A small amount of FC170 surfactant (3M) was added to adjust adhesion. The dried coating weight of the polyamide layer D was 0.19 mg/cm^2. The multilayer sheet D-E was laminated to the multilayer sheet A-B-C such that layer D contacted layer C. The final multilayer structure was 67 mil (1.7 mm) thick.

Example 4

A 7 mil (0.18 mm) polyester film (A) was corona treated and primed with CX-100. A 28 mil (0.71 mm) curable polyurethane elastomer (B) was reaction extruded onto the primed film. This polyurethane was cured first by an electron beam through the polyester and then by top exposure to ultraviolet radiation for 30 seconds until cured. A second layer (C) of 27 mils (0.69 mm) of curable polyurethane elastomer was then laminated to layer B.

An antistatic layer (E) was coated to a 4 mil (0.1 mm) polyester film (F). An additional radiation curable pigment layer (D) was added on top of layer E. This multilayer material was then laminated to the above flexible plate so that layers D and E contacted each other.

The polyurethane layers C and D were of the same composition. To form these layers 62.5 parts by weight of a polyol stream was mixed with 37.5 parts of 4,4-bis(isocyanato cyclohexyl methane) in a twin screw extruder and extruded as a thin film. The polyol stream contained the following components (in parts by weight):

286.1 parts of 1000 MW poly 1,2-(butylene oxide) diol
32.8 parts of 1,4 butane diol
10.7 parts of 2-glycerol methacrylate
10.6 parts of IRGACURE 651 (free radical initiator)
0.1 part methylene blue
0.06 part ferric chloride
0.26 part dibutyl tin dilaurate.

The radiation curable pigmented hardcap layer D was prepared by combining the following materials in solution:

a. 300 parts of methyl ethyl ketone solution at 30% by weight solids of a methacrylate functional polyvinyl chloride copolymer;

b. 300 parts of a methyl ethyl ketone solution at 30% by weight solids of a methacrylate functional polyurethane resin containing 36% by weight hard segments consisting of 1,4-butane diol, 1-glycerol methacrylate and 4,4-bisisocyanato cyclohexyl methane;

c. 3 parts of IRGACURE 369 (Ciba-Geigy) photoinitiator;

d. 350 parts of methyl ethyl ketone solvent;

e. 50 parts of a pigment dispersion consisting of 10 parts of SUN-234 magenta (Sun Chemical Co.) pigment, 10 parts of methacrylated PVC copolymer solution described in a. above and 30 parts of methyl ethyl ketone solvent. This dispersion was prepared by sand milling this mixture until no particles larger than 10 microns were apparent.

These materials were blended using a high speed mixer. The radiation curable pigment layer was then applied to the 4 mil (0.1 mm)

polyester film in sufficient thickness so as to provide a coating which after oven drying had a weight of .54 mg/cm^2.

Example 5

The flexible plate produced in Example 4 was image exposed to ultraviolet radiation through a negative image bearing film after removal of the 4 mil (0.1 mm) polyester cover layer. Exposure times were 3 minutes for reverse images and 9 minutes for all other images. Six thermal development contacts were made at process temperatures of 175°C/60°C (respectively for the elements carrying the absorbent material and the flexographic plate). The flexographic printing plate exhibited a very clean floor with 27 mil (0.69 mm) relief and 28 mil (0.71 mm) floor.

Example 6

A roll of 7 mil (0.18 mm) polyethylene terephthalate (PET) film having a width of 27 inches (68.6 cm) and annealed according to WO 91/14603, hereinafter referred to as the substrate, was corona treated in air. The treated substrate film was coated with a 0.3% solids solution of CX-100 (an aziridine functional compound available from Polyvinyl Chemical Co.) in isopropyl alcohol. The coated substrate film was dried at a temperature between 250 and 260°F (121 and 127°C) for 1 minute to provide a coating thickness of several hundred Angstroms. This coated substrated will be referred to hereinafter as Layer A.

A photosensitive floor layer was coated onto the aziridine coating of Layer A. The components of the floor and their respective amounts, are set forth as follows:

68.5% Kraton 1119, a styrene/isoprene/styrene block copolymer available fro Shell Chemical Co.

20.5 % LIR-390, an isoprene/butadiene block copolymer from Kuraray Co. Ltd.

7.5 % Sartomer 349, a diacrylate of ethoxylated bisphenol a available from Sartomer Company

1.0 % Sunlite 666, a wax from Sun Chemical Company, Indistries

2.0 % Ingracure 651, 2,2-dimethoxy-2-phenyl acetophenone from Ciba-Geigy Corp.

0.5 % Irganox, a phenolic type anitoxidant from Ciba-Geigy Corp.

Specifically, the components of a photosensitive floor layer were blended in a Leistritz counter-rotating twin screw extruder having a length of approximately 104 inches (260 cm) a screw diameter of 2.64 inches (6.7 cm) and nine heated zones [zone 1 at 160°F(, zone 2 at 350°F, and zones 3-9 at 330°F, and extruded directly onto Layer A at a rate of 150 lbs./hour (68.0 kg/hour) and a web speed of 7.2 feet/minute (2.2 meters/minute). A silicone treated PET cover film, having a thickness of 5.0 mils (0.13 mm), was placed on top of the extrudate just before it was passed between two nip rollers. The two nip rolls were maintained at 150°F (66°C) set to have a gap of 29 mils (0.7 cm) greater than the sum of thicknesses of the PET substrate and PET cover film. Downweb, after the sandwich had passed through the nip rollers and cooled, the silicone treated PET cover film was removed and a silicone treated polypropylene cover film, having a thickness of 3 mils (0.076 mm) was put down over the extrudate layer in its place.

The extrudate was then exposed to ultraviolet (UV) irradiation about 30 feet (9.14 meters) downweb from the nip rollers, using top and bottom banks of directly opposing Sylvania BL fluorescent lamps to cure the photosensitive composition. The average intensity of the radiation was 15 mW/cm^2 [as measured using a Model PP2000 Power Puck instrument sold by EIT, Inc. using a Channel A bandwidth of 320-390 nm and a one minute exposure time], and the exposure time was 8.4 seconds. This

cured composition, having a thickness of about 31 mils (0.79 mm), will be hereinafter referred to as Layer B, or the floor layer.

A second photosensitive composition was prepared using the components and amounts shown below:

57.5 % KRATON 1117, (added as a 30% (w/w) solids solution in toluene);

32.5% PolyBD R-45VT, a divinyl terminated polybutadiene oligomer from EIF Atochem No. America, Inc.;

7.5% Sartomer 349, a diacrylate of ethoxylated bisphenol a available from Sartomer Company; and

2.5% Ingracure 651, 2,2-dimethoxy-2-phenyl acetophenone from Ciba-Geigy Corp.

Specifically, the components were mixed in a 1 quart glass jar in toluene to give about a 43.0% solids solution. The jar was placed on a roller mill overnight to achieve complete dissolution and mixing. After removal from the roller mill, the solution was allowed to stand for about 2 hours. The solution was then knife coated through a 30 mil (0.76 mm) gap onto a silicone treated calendared paper liner having a thickness of 4.5 mils (0.114 mm), and dried overnight at room temperature followed by 30 minutes at 160°F (71°C) in a forced air oven. The dried film thickness of this unimaged composition was about 10 to 11 mils (0.25 to 0.28 mm).

Next, after removal of the polypropylene cover film from Layer B, a sheet of the second photosensitive film composition was laminated to Layer B using a Model 447 MATCHPRINT laminator (3M Company, St. Paul, MN) and, after cooling to room temperature, the silicone treated calendared paper liner was removed. The top roll temperature of the laminator was set at 200°F (93°C), the bottom roll temperature was set at 100°F (38°C) and the line speed through the laminator was 26.1 inches/minute (66.3 cm/minute). This procedure was repeated twice more to provide a combined thickness of the three laminated layers of the

unimaged film composition of about 32 mils (0.81 mm). This combined layer of film will be hereinafter referred to as Layer C.

A film of MELINEX 377, (a polyethylene terephthalate film from ICI), having a thickness of 5 mils (0.13 mm) and having a matte surface, hereinafter referred to as Layer E, was coated on the matte surface with an aqueous dispersion containing 0.1% (w/w) of TRITON X-100 surfactant and 0.1% vanadium pentoxide (w/w) and dried at 212°F (100°C) for 1 minute to give a final coating weight of 3.25 mg/ft.^{2} (35 mg/m^2). The vanadium pentoxide was prepared as described in U.S. Patent No. 5,322,671 (Col. 37, Example 1).

Next, an 8% solids solution of MACROMELT 6200 (a polyamide compound available from Henkel Chemical Co.) in a solvent mixture of n-propyl alcohol:toluene/70:30 (w/w) containing a small amount of FLUORAD FC170 (3M Company) surfactant to adjust adhesion was coated on top of the vanadium pentoxide. The coating of MACROMELT 6200 was dried in a forced air oven at 160°F (71°C) for one minute to provide a coating weight of 125 mg/ft.^{2} (1300 mg/m^2). This layer will hereinafter be referred to as Layer D.

The Layer D/Layer E combination was laminated to Layer C, such that Layer D was between Layers C and E, using a MATCHPRINT laminator as described above except the speed was set at 32 inches/minute (81.3 cm/minute), to give a multilayer imageable flexographic plate. Next the imageable multilayer plate was placed in a platen press whose top platen had been preheated to 290°F (143°C), two steel shims having a thickness of 0.071 inches (1.80 mm) were placed on opposite sides of the multilayer plate, and a 0.007 inch (0.18 mm) thick PET film was placed over the multilayer plate and adjacent shims. The press was closed and a pressure of 80 psi (0.55 MPa) was applied. After 1 minute under these conditions the press was opened, the sample removed and allowed to cool. In this manner an imageable multilayer

flexographic plate having a uniform total thickness (not including Layer E) of about 69 mils (1.75 mm) was produced.

Example 7

The multilayer plate of Example 6 was image-wise irradiated to image-wise cure Layer C, and thermally developed to provide flexographic printing plates having a relief surface. Specifically, Layer D of Example 6 was placed in contact with a film bearing the negative image of a test pattern, positioned in the vacuum exposure frame of an unaltered factory Kelleigh Model 250 flexographic plate processor and irradiated under vacuum of 25 inches (635 mm) of Hg from the top side only with fluorescent black phosphor lights having a maximum intensity of emission between 360 and 365 nm. The average intensity of the radiation was 22.5 mW/cm^2 as measured using the Model PP2000 Power Puck and conditions described in Example 6. The duration of exposure was 15 minutes.

After irradiation the imaged multilayer plate was thermally developed, to remove the unexposed regions of Layer C and the part of Layer D which was over these regions, using a processor of the type described in U.S. Patent No. 5,279,697. The circumferential speed of the processor was fixed internally at 30 inches/minute (76.2 cm/minute). The infrared (IR) preheat lamp was set to 50% of full power; the temperature of the roll supporting the multilayer plate was set at 72°C; the temperature of the developing roll bearing the absorbent material was set at 140°C; and six passes (each pass being against fresh absorbent material) were used to thermally develop the plate. CEREX Type 23, a spunbonded 6,6 nylon nonwoven material from CEREX America, Inc., was employed as the absorbent on the developer roll. The resulting imaged, thermally developed multilayer plate comprised a cured Layer B having a thickness of 0.031 inches (0.79 mm) and a cured Layer C relief surface having a thickness of 0.032 inches (0.81 mm).

Following this thermal development step, the imaged multilayer plate was finished by further exposing the plate to irradiation in the second chamber of the processor to cure trace amounts of unexposed, unremoved Layer C and detackify the plate surface. This chamber was equipped with both germicidal and black phosphor fluorescent lights which were operated simultaneously. The duration of exposure was 9 minutes.

The imaged, thermally developed multilayer plate was evaluated visually at a magnification of 40X for the completeness of removal of regions of unexposed Layers C and D, as well as the overall appearance of the relief features in Layer C. The plate of this example showed complete removal of unexposed regions of Layers C and D as well as overall good definition of the features of Layer C.

Examples C1 and C2

Examples 6 and 7 were repeated, except that a different formulation was used for Layer C as follows:

57.5% Kraton 1117

40% PolyBD R-45VT

2.5% Irgacure 651

The resulting thermally developed plate made using the vinyl terminated oligomer "PolyBD R-45VT" (in the absence of a diacrylate compound such as Sartomer 349) did not give an acceptable multilayer flexographic plate. Although some curing of Layer C had taken place in the imaged regions, it was insufficient to provide a plate having adequate image definition after thermal development, and thus could not be satisfactorily utilized in a flexographic printing process.

What is claimed is:

1. A process for producing a multilayer, flexible photosensitive plate comprising (i) applying a first photosensitive elastomeric layer to a flexible substrate, (ii) curing the first photosensitive elastomeric layer by exposure to actinic radiation, and (iii) following curing of the first layer, applying a second layer, which is at least 0.2 mm thick, onto the first photosensitive layer, the second layer comprising a photosensitive elastomeric composition having no more than 1% by weight ethylenically unsaturated copolymerizable molecules with molecular weights less than 300.

2. The process according to claim 1 wherein said first photosensitive elastomeric layer comprises first and second major surfaces and said curing step (ii) comprises the exposure of said first and second major surfaces of said first photosensitive elastomeric layer to actinic radiation.

3. The process according to claim 1 wherein said second layer comprises an oligomer having more than one ethylenically unsaturated group.

4. The process according to claim 1 wherein said second layer comprises:

(X) 20 to 80 parts by weight thermoplastic elastomeric ABA type block copolymer,

(Y) 10 to 50 parts by weight of an oligomer having more than one ethylenically unsaturated group, and

(Z) 0.5 to 5 parts by weight photoinitiator.

5. The process according to claim 1 wherein said first photosensitive elastomeric layer comprises:

(A) 20 to 90 parts by weight thermoplastic elastomeric ABA type block copolymer,

(B) 3 to 50 parts by weight crosslinking agent having an average of more than 1.3 ethylenically unsaturated groups per molecule, and

(C) 0.5 to 5.0 parts by weight photoinitiator.

6. The process according to claim 4 wherein said oligomer (Y) has more than one vinyl group.

7. The process according to claim 4 wherein said oligomer (Y) has more than one acrylate group.

8. The process according to claim 4 wherein said oligomer (Y) contains less than 500 parts per million unreacted monomer.

9. The process according to claim 4 wherein said oligomer (Y) has a molecular weight greater than 1000.

10. The process according to Claim 6 wherein said second layer additionally comprises a second crosslinking agent having more than one acrylate group and a molecular weight between 300 and 1000.

11. A multilayered, flexible phtosensitive plate comprising:

(A) a flexible substrate,

(B) a first photosensitive elastomeric layer which has been cured by exposure to actinic radiation, and

(C) a second photosensitive elastomeric layer at least 0.2 mm thick comprising no more than 1% by weight ethylenically unsaturated molecules with molecular weights less than 300.

12. The plate according to Claim 11 wherein said first photosensitive elastomeric layer comprises first and second major surfaces and was cured by the exposure of said first and second major surfaces to actinic radiation.

13. The plate according to claim 11 wherein said second layer comprises an oligomer having more than one ethylenically unsaturated group.

14. The plate according to claim 11 wherein said second layer comprises:

(X) 20 to 80 parts by weight thermoplastic elastomeric ABA type block copolymer,

(Y) 10 to 50 parts by weight of an oligomer having more than one ethylenically unsaturated group, and

(Z) 0.5 to 5 parts by weight photoinitiator.

15. The plate according to claim 11 wherein said first photosensitive elastomeric layer comprises:

(A) 20 to 90 parts by weight thermoplastic elastomeric BA type block copolymer,

(B) 3 to 50 parts by weight crosslinking agent having an average of more than 1.3 ethylenically unsaturated groups per molecule, and

(C) 0.5 to 5.0 parts by weight photoinitiator.

16. The plate according to claim 14 wherein said oligomer (Y) has more than one vinyl group.

17. The plate according to claim 14 wherein said oligomer (Y) has more than one acrylate group.

18. The plate according to claim 14 wherein said oligomer (Y) contains less than 500 parts per million unreacted monomer.

19. The plate according to claim 14 wherein said oligomer (Y) has a molecular weight greater than 1000.

20. The plate according to claim 16 wherein said second layer additionally comprises a second crosslinking agent having more than one acrylate group and a molecular weight between 300 and 1000.

21. A process for producing a multilayered flexographic printing plate comprising:

(i) applying a first photosensitive, elastomeric layer to a flexible substrate,

(ii) curing the elastomeric composition by exposure to radiation,

(iii) applying a second layer at least 0.2 mm thick onto the first elastomer layer, the second layer comprising a photosensitive curable elastomer composition having no more than 1% by weight ethylenically unsaturated copolymerizable molecules with molecular weights less than 300,

(iv) image-wise exposing the second photosensitive, elastomeric layer to ultraviolet radiation, and

(v) developing the printing plate by contacting the image-wise exposed photosensitive elastomeric layer with an absorbent material at a temperature sufficient to enable unexposed portions of the photosensitive layer to flow into the absorbent layer.

22. The process according to claim 21 wherein said first photosensitive elastomeric layer comprises first and second major surfaces and said curing step (ii) comprises the exposure of said first and second major surfaces of said first photosensitive elastomeric layer to actinic radiation.

23. The process according to claim 21 wherein said second layer comprises an oligomer having more than one ethylenically unsaturated group.

24. The process according to claim 21 wherein said second layer comprises:

(X) 20 to 80 parts by weight thermoplastic elastomeric ABA type block copolymer,

(Y) 10 to 50 parts by weight of an oligomer having more than one ethylenically unsaturated group and having a molecular weight greater than 1000, and

(Z) 0.5 to 5 parts by weight photoinitiator.

25. The process of claim 21 wherein said first photosensitive elastomeric layer comprises:

(A) 20 to 90 parts by weight thermoplastic elastomeric ABA type block copolymer,

(B) 3 to 50 parts by weight crosslinking agent having an average of more than 1.3 ethylenically unsaturated groups per molecule, and

(C) 0.5 to 5.0 parts by weight photoinitiator.

26. The process of claim 24 in which the oligomer (Y) contains less than 500 parts per million unreacted monomer.

27. The process of claim 24 in which the oligomer (Y) has a molecular weight greater than 1000.

28. A flexographic printing plate comprising a substrate, a floor layer in which the degree of cure is constant in a plane perpendicular to the substrate, and an image bearing relief layer.

29. The flexographic printing plate of claim 28 wherein the image bearing relief layer has a degree of cure at the interface with the floor layer which is different from the degree of cure of said floor layer at said interface.

30. The flexographic printing plate of claim 29 in which the floor layer comprises the cured product of the following reactants:

(A) 20 to 90 parts by weight thermoplastic elastomeric ABA type block copolymer,

(B) 3 to 50 parts by weight crosslinking agent having an average of more than 1.3 ethylenically unsaturated groups per molecule, and

(C) 0.5 to 5.0 parts by weight photoinitiator,

and the image bearing relief layer comprises the cured product of the following reactants:

(X) 20 to 80 parts by weight thermoplastic elastomeric ABA type block copolymer,

(Y) 10 to 50 parts by weight of an oligomer having more than one ethylenically unsaturated group, and

(Z) 0.5 to 5.0 parts by weight photoinitiator.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/01257

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G03F7/11 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 665 469 A (MINNESOTA MINING & MFG) 2 August 1995 see the whole document ---	1-30
X	US 3 287 152 A (F.P. ALLES) 22 November 1966 see the whole document ---	1
A	WO 92 21068 A (MINNESOTA MINING & MFG) 26 November 1992 see the whole document ---	1
A	US 5 015 556 A (MARTENS JOHN A) 14 May 1991 cited in the application see the whole document --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Rasschaert, A

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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